

# Volumetric properties of concentrated electrolyte solutions

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The paper presents a brief review of the current views, theories, and models in the field of molar volumes of highly concentrated electrolyte solutions. A comparison with dilute solutions is made in terms of the composition dependence of the molar volume of solutions, and the specificity of concentrated solutions is pointed out.

В статье приводится краткий обзор современных воззрений, теорий и моделей в области мольных объемов высококонцентрированных растворов электролитов. На основании обсуждения зависимости мольных объемов растворов от их состава проведено сравнение с разбавленными растворами и подчеркнута специфичность концентрированных растворов.

The volumetric properties of solutions are a basic source of information on the structure and on interactions between the components in solutions. These properties include the density and the molar volume of solutions, as well as the coefficients in equations for the molar volume as a function of temperature and pressure. These characteristics depend on both the temperature and the composition of solutions, and these dependences are an additional source of information. Moreover, the volumetric properties are an attractive subject to study because of the relative ease with which the density from which all the other characteristics are derived, can be determined experimentally.

In the case of electrolyte solutions, it is customary to distinguish between the solvent and the solute. This distinction is made for two main reasons. One of these is the composition of electrolyte solutions. In studies of the properties of electrolyte solutions, the situation most frequently encountered is that in which the electrolyte, *i.e.* the solute, constitutes only a small fraction of the total amount of solution. Accordingly, the composition of solutions is usually expressed in terms of the amount of electrolyte either per unit volume of solution ( $c$ ) or per unit amount of solvent ( $m$ ). However, compositions such that the solvent predominates over the solute are not the rule and systems are commonly studied in which the solubility of electrolytes is high enough for solutions to be prepared at concentrations where the amount of solute is comparable with that of solvent.

The other reason for making the distinction between solvent and solute lies in the

physical processes that occur at the act of forming the solution. The substance being dissolved, the electrolyte, is usually solid at the temperature of the formation of solution, and on mixing with the solvent it is partially or completely broken up into ions or other charged species. Thus the solute is at least partly ionic in nature, in contrast to the molecular character of the solvent. If the solvent molecules are polarized by interaction with the dissolved ions to a point where their dissociation occurs, it is more appropriate to speak of a mixture of molten ionic salts.

From the above division it will be clear what is meant by saying that the volumetric behaviour of substances in solution provides information on the solute—solvent, solute—solute, and solvent—solvent interactions.

The density of solutions ( $\rho$ ) is mostly the primary experimental quantity; the measured data are correlated and used to calculate other thermodynamic quantities. The temperature dependence of density is usually expressed in the form

$$\rho = a + bt + ct^2 \quad (1)$$

where  $t$  is the temperature, and  $a$ ,  $b$ , and  $c$  are empirical parameters. A characteristic feature of the temperature dependence is that the quadratic term  $ct^2$  is of little weight only, allowing eqn (1) to be used to extrapolate the density beyond the temperature range covered by experimental data with fairly good reliability.

The dependence of the density on the electrolyte concentration is merely an empirical approximation of no great thermodynamic significance. The same applies to the calculations of densities of more complicated systems on the basis of densities of the components.

The molar volume ( $V_m$ ) is calculated from experimental data for the density,  $V_m = (M_1x_1 + M_2x_2)/\rho$ . This equation implies that, if the temperature dependence of density is approximated by a linear relationship, then the molar volume cannot be related to temperature by an analogous linear equation. Unfortunately, the opposite treatment has been quite common [1—4].

The composition dependence of the molar volume is an important source of information on the thermodynamic behaviour of solutions and may be used to verify models of solution structure. From both the methodological and historical viewpoints, two main approaches to the problem can be traced. By studying either the molar volumes at infinite dilution of an electrolyte in solution or the partial molar volumes in very dilute solutions where the interactions between ions can be ignored, information can be obtained about the solvent and the ion—solvent interactions. It is possible to assess the influence of ions on the structure of a solvent, to compare the electrolyte—solvent interaction strengths for various electrolytes by comparing the “energies of transfer”, to split the quantities characterizing the electrolyte—solvent interactions into ionic contributions, and to compare the solvation and coordination numbers as well as a number of other

quantities. Studies of this kind are numerous and have been reviewed in some monographs [5—7].

The study of molar volumes in highly concentrated solutions provides information on the ion—solvent and ion—ion interactions, while the solvent—solvent interactions can in most cases be neglected. At such solvent concentrations that do not permit complete filling of the primary solvation spheres of ions, there is preferential solvation of the most strongly polarizing species in solution, usually the cation. The interaction between strongly polarizing ions and a solvent resulting in the formation of solvated ions causes changes not only in the structure of solution but also in the shape, volume, and orientation of solvent molecules. In describing concentrated solutions, one cannot therefore adhere to the same concepts and use the same relations as in treating dilute solutions.

The total volume,  $V$ , and the molar volume (mean molar volume) of solution,  $V_m$ , are given by

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad (2)$$

$$V_m = x_1 \bar{V}_1 + x_2 \bar{V}_2 \quad (3)$$

The partial molar volume of component  $i$ ,  $\bar{V}_i$ , is defined as the volume change that occurs on addition of one mole of the component to an amount of solution sufficiently large so that its concentration is not altered

$$\bar{V}_i = (\partial V / \partial n_i)_{T,p,n_{j \neq i}}$$

The partial molar volumes are experimentally accessible only at the end points of the concentration scale, *i.e.* for pure components, since here the partial molar volume of a component is equal to its molar volume.

$$V_2^\circ = \bar{V}_2 = (\partial V / \partial n_2)_{T,p,n_1=0} \quad (4)$$

$$V_1^\circ = \bar{V}_1 = (\partial V / \partial n_1)_{T,p,n_2=0}$$

In contrast to  $V_2^\circ$ , the molar volume of a pure solvent,  $V_1^\circ$ , is a readily accessible quantity since solvents, unlike electrolytes, are liquid at the temperature of measurement (ranging usually between 0 and 100 °C). The calculation of the partial molar volume, which depends on the composition of solution, is rather laborious, and therefore some auxiliary quantities have been introduced.

In the region of dilute solutions, such a quantity is the apparent molar volume of electrolyte,  $\Phi_V$ , defined in parallel to a number of thermodynamic quantities by the expression

$$V = n_1 V_1^\circ + n_2 \Phi_V \quad (5)$$

Compared with eqn (2), the volume of only one of the components making up the solution depends on the solution composition, and this somewhat facilitates further treatment based on eqn (5). The apparent molar volume can be calculated in a straightforward way from experimentally determined density of solution by using the relation

$$\Phi_v = \frac{1}{n_2} \left( \frac{n_1 M_1 + n_2 M_2}{\rho} \right) - n_1 V_1^\circ \quad (6)$$

In the limit as  $n_2 \rightarrow 0$ , the apparent molar volume equals the partial molar volume of electrolyte at infinite dilution,  $V_2^\infty$ , and is also denoted by the symbol  $\Phi_v^\circ$ . The apparent molar volume of electrolyte says nothing about the effective molar volume of electrolyte or about the molar volume of pure component 2, and incorporates all volume changes on mixing components 1 and 2. This is why the apparent molar quantities have little application in thermodynamics, but are used occasionally as auxiliary quantities in calculations of partial molar quantities.

Three relationships have been proposed to describe the concentration dependence of the apparent molar volume. According to *Masson* [8],  $\Phi_v$  increases linearly with the square root of the concentration of component 2

$$\Phi_v = \Phi_v^\circ + a\sqrt{c} \quad (7)$$

where  $a$  is the slope determined on the basis of experimental data. This originally empirical equation was later derived from the Debye—Hückel limiting law and is, therefore, also a limiting expression. The parameter in the square root term is not an empirical but a theoretically based parameter which depends on the type of electrolyte only and not on a particular composition. In order to obtain full agreement with experimental data, *Redlich* and *Meyer* [9] proposed an equation of the form

$$\Phi_v = \Phi_v^\circ + S_v\sqrt{c} + bc \quad (8)$$

where  $S_v$  is the theoretical limiting slope. This relation is adequate for most  $A_1B_1$  and some  $A_2B_1$  electrolytes, but deviations have been found for some  $A_2B_1$  and also for  $A_3B_1$  and  $A_4B_1$  electrolytes. A more complex equation involving more parameters has therefore been proposed by *Owen* and *Brinkley* [10] for polyvalent salts. Because of its complexity, however, this equation has not been widely used.

The calculation of  $\Phi_v^\circ$  from the concentration dependence of  $\Phi_v$  is based on the use of the limiting slope  $S_v$  in connection with the Redlich—Meyer equation. This equation is, however, adequate only up to 70 °C and the measurement must be made in as dilute solutions as possible in order for the error to be a minimum. For higher temperatures, the *Masson* equation is used, but the values of  $\Phi_v^\circ$  are subject

to errors as high as  $3 \text{ cm}^3 \text{ mol}^{-1}$ . The constant  $a$  in the Masson equation reflects ion—ion interactions at increased electrolyte concentrations.

In the region of dilute solutions, the apparent molar volume of electrolyte has proved to be useful in studying the ion—solvent interactions. At infinite dilution, where  $\Phi_v = \Phi_v^\circ = V_2^\circ$  it may be assumed that ions exert no influence on one another and therefore the  $V_2^\circ$  for an electrolyte, e.g.  $V_{MX}^\circ$ , is equal to the sum of the corresponding ionic volumes,  $V_{M^+}^\circ$  and  $V_{X^-}^\circ$ . A study of the dependence of  $V_{ion}^\circ$  on the ionic charge and size, temperature, the kind of solvent, etc., may provide information on the ion—solvent interactions. There is, however, the problem of assigning values to the  $V^\circ$  of the individual ions. The division of the  $V_{MX}^\circ$  into its ionic components can only be made on extrathermodynamic grounds. The situation is further hampered by lack of knowledge of some parameters of ions (such as the radius). A number of methods have been proposed for normalizing the  $V_{ion}^\circ$ ; the details are given in monographs and original papers [5—7, 11].

Čeleda starts in his model [12, 13] from the empirical equation of Masson (7) and assumes that this equation holds over the whole concentration range up to the anhydrous molten salt. He circumvents the problem of determining the constant  $a$  in eqn (7) by assuming that, at a certain concentration, the product  $\Phi_v c = 1$ , i.e. the volume is completely filled with the electrolyte. He denotes the concentration by the symbol  $c_0$  and the electrolyte volume by  $V_2^\circ$ . Thus,  $V_2^\circ c_0 = 1$ , and eqn (7) can be rewritten in a form where the constant  $a$  does not occur explicitly

$$\Phi_v = \Phi_v^\circ + (V_2^\circ - \Phi_v^\circ) \left( \frac{c}{c_0} \right)^{1/2} \quad (9)$$

However, a number of data sets obtained in the region of highly concentrated solutions [14—17] indicate that the assumption of the validity of eqn (7) over the whole concentration range from dilute solutions to fused salts is not justified.

The choice of the method of treating experimental data for the region of dilute solutions usually depends on the results to be obtained. Experimental data on density are used to calculate the apparent molar volumes of electrolyte and these are correlated with the solution composition. The partial molar volumes  $\bar{V}_1$  and  $\bar{V}_2$  are obtained by differentiating an equation for  $\Phi_v$  as a function of  $m$  or  $m^{1/2}$ . The same results should be obtained by treating the experimental data in the  $V_m - x_2$  coordinate system. However, the use of the former coordinate system is more advantageous since the  $\Phi_v$  against  $m$  or  $m^{1/2}$  plot exhibits smaller deviations from linearity. Practical experience shows that the differentiation introduces a considerable degree of uncertainty into the results, by no means permitting reliable extrapolation of the  $\bar{V}_i$  values beyond the range of experimental observation. Hence it is clear that these methods do not provide a route for obtaining values of  $V_2^\circ$ , the molar volume of pure electrolyte in the hypothetical undercooled state, from experimental data on density of dilute and concentrated solutions.

New problems arise in the region of concentrated solutions. The dominant factors determining the solution structure in this region are ion-solvent and ion-ion interactions, and the formation of contact ion pairs. It is clear that the relations derived for the region of dilute solutions cannot hold under these conditions. The region of concentrated solutions is usually discussed in terms of deviations from the principle of additivity; on closer examination it turns out that, in fact, two questions are involved: deviations from additivity in the systems electrolyte + solvent, and deviations from additivity in mixtures of molten hydrates or solvates.

In the first case, we are dealing with deviations of real systems from eqn (2) where the partial molar volumes of components, which are concentration dependent, are replaced by the molar volumes of pure components at the temperature of the experiment. When formulated in this manner, the problem relates to the mixing of an electrolyte with a molecular solvent and in this situation one does not intuitively expect the additivity of molar volumes. Moreover, the molar volume of the electrolyte in the liquid state,  $V_2^0$ , at the temperature of the experiment is usually unknown. For these reasons, the problem is usually treated in terms of the dependence of the molar volume of solution on the electrolyte concentration.

Viewing the solution as a system formed by mixing components 1 (solvent) and 2 (electrolyte), we can state on the basis of eqn (3) that, if the net molar volume of the solution is a linear function of the mole fraction of either component ( $x_1$  or  $x_2$ ), then the partial molar volumes of the two components in the solution are always equal to the molar volumes of pure components ( $\bar{V}_1 = V_1^0$ ,  $\bar{V}_2 = V_2^0$ ) irrespective of the composition of the solution. This implies that the two components exert no influence on each other and that there are no volume changes due to the spatial geometry factors. Additivity in this case means ideality of the system in regard of the volumetric properties.

Information on the behaviour of non-ideal systems (solutions) is obtained from the dependences of the partial molar volumes of the two components on the solution composition. In dilute electrolyte solutions,  $\bar{V}_1$  is usually constant whereas  $\bar{V}_2$  depends strongly on the electrolyte concentration. Accordingly, the volumetric properties in this concentration range are discussed in terms of the apparent molar volume of salt,  $\Phi_v$ . As the salt concentration increases, the partial molar volumes of both components become strongly dependent on the solution composition, and in very concentrated solutions there is often a clear tendency towards a behaviour exactly opposite to that observed for dilute solutions.

Equation (3) is a purely thermodynamic relationship; it describes rigorously the composition dependence of the molar volume of solution but gives no idea about interactions in solution and cannot be used to test structural models of solutions. An approach is therefore frequently used in which the volume changes on mixing pure components are expressed in terms of the excess molar volume

$$V_m^E = x_1(\bar{V}_1 - V_1^\circ) + x_2(\bar{V}_2 - V_2^\circ) = V_m - x_1 V_1^\circ - x_2 V_2^\circ \quad (10)$$

and changes in this quantity with changing composition are discussed in relation to interactions and structural models of solutions. In the case of concentrated solutions, it is convenient to study the composition dependence of the volumetric properties using the  $V_m$ — $x_2$  coordinate system, since the use of the molarity and molality concentration scales is impracticable or impractical for solutions the compositions of which approach pure molten component 2.

Both positive and negative deviations from additivity have been observed for mixtures of two molten electrolytes, *i.e.* for anhydrous molten salt systems [18, 19]. The positive deviations have been attributed to compound formation, and the negative deviations are due to the local arrangement of the crystal field and to van der Waals interactions. Binary electrolyte—solvent solutions have been found to exhibit only negative deviations from additivity, arising from interactions between the electrolyte ions and the solvent molecules. Each ion in solution is surrounded (solvated) by solvent molecules which are influenced by the ion. The tendency towards negative deviations is very pronounced in aqueous solutions as a consequence of the disturbance of the specific noncompact structure of pure water by the ions. For example, the partial molar volume of water in the melt  $\text{LiNO}_3$ — $\text{KNO}_3$ — $\text{H}_2\text{O}$  at 119°C is  $16.3 \text{ cm}^3 \text{ mol}^{-1}$ , whereas  $V_1^\circ$  obtained by extrapolation to the same temperature is  $19 \text{ cm}^3 \text{ mol}^{-1}$  [20].

Several models have been proposed to account for this behaviour. *Tammann* [21] was the first to advance the hypothesis that in the presence of an ionized electrolyte water behaves as if it experienced a constant pressure over and above the atmospheric pressure. In this approach, the volume change associated with mixing (dissolution) is ascribed to a compression of water in solution rather than to changes in the properties of the electrolyte. Using this concept and a relation of *Tait* [22], *Gibson* [23] derived an expression for the molar volume of solvent in solution at pressure  $p$

$$V_1 = V_1^\circ \left( 1 - C \log \frac{B + p + p_E}{B + p_0} \right) \quad (11)$$

where  $B$  and  $C$  are constants characteristic of the solvent,  $p_0$  is the initial pressure (1 atm), and  $p_E$ , the only parameter depending on the properties of the solution, can be calculated from compressibility measurements. Using eqn (11), the molar volume of solution or of pure electrolyte (in the liquid state) can be evaluated from the relation  $V_m = x_1 V_1 + x_2 V_2^\circ$ . With the  $p_E$  parameter obtained as indicated above, *Gibson* [23] calculated molar volumes of pure salts  $\text{KX}$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) in the liquid state and found them to be independent of the electrolyte concentration in solution.

Using as the starting point the above given dependence of the partial molar

volumes of solvent and electrolyte on the composition, *Kodejš* and *Sláma* [24] introduced the apparent molar volume of solvent,  $V_1$ , as a composition dependent quantity while considering the partial molar volume of electrolyte to be constant and equal to the molar volume of pure component 2. The molar volume of solution is then given by

$$V_m = x_1 V_1 + x_2 V_2^{\circ} \quad (12)$$

On the formal side, this equation is comparable to eqn (5), since in both cases one of the molar volumes is taken as independent of the solution composition. Mathematically, the two approaches are analogous in that both express the composition dependence of the excess molar volume. The only difference is that each of them includes the experimentally found excess molar volume with the molar volume of a different component of the solution. Each approach is justified within the mole fraction range for which it is used, though in the light of results obtained by other experimental techniques the approach based on eqn (12) appears to be applicable over a wider range of composition.

The same authors [24] describe the behaviour of real systems by the equation

$$V_m = x_2 V_2^{\circ} + x_1 \left( A + \frac{CR}{D+R} \right) \quad (13)$$

where  $R$  is the molar solvent to electrolyte ratio ( $R = x_1/x_2$ ), and  $A$ ,  $C$ , and  $D$  are empirical parameters.

In a similar approach, *Kodejš* and *Sacchetto* [25] calculated the apparent molar volume of solvent,  $V_1$ , in eqn (12) from values of  $V_1^{\circ}$  and  $V_1^{\infty}$  by invoking the concept of a distribution of solvent molecules between two types of site in the solution structure to which two magnitudes of the molar volume of solvent,  $V_1^{\circ}$  and  $V_1^{\infty}$ , are assigned. The calculation of the distribution of solvent molecules between the two types of site makes use of the concepts of the quasi-lattice theory of melts and takes into account the strength of the solvent—electrolyte interaction expressed in terms of  $\Delta H_{tr}$ , the enthalpy change associated with the transfer of the solvent from the bulk phase into its infinitely dilute solution in molten electrolyte at the temperature of measurement (a hypothetical undercooled solution). The values of  $\Delta H_{tr}$  can be evaluated from vapour pressures of solvents above concentrated solutions of electrolytes by using the theory of *Stokes* and *Robinson* [26]. The model is in good agreement with experimental data and allows the  $V_2^{\circ}$  to be calculated as a parameter of an equation for the molar volume of solution as a function of the electrolyte concentration

$$V_m = x_2 V_2^{\circ} + \left[ \frac{\beta\Theta}{1+x_2(\beta\Theta-1)} V_1^{\infty} + \frac{1}{1+x_2(\beta\Theta-1)} V_1^{\circ} \right] x_1 \quad (14)$$

where  $\beta = \exp(-\Delta H_{tr}/ZRT)$ , and  $\Theta = Z_1/Z_2$  is the ratio of the coordination



number of a solvent molecule in the pure solvent to the coordination number of an ion in the melt. Good agreement has been found between values of the parameter  $V_2^*$ , the molar volume of a hypothetical undercooled molten electrolyte, obtained from the above approach and by extrapolation of densities from the region of molten anhydrous salts. A disadvantage of eqn (14) is that it requires the knowledge of the values of  $\Delta H_{tr}$ , which are generally difficult to obtain. The validity of the model is restricted to the region of concentrated solutions, where the derivation of eqn (14) is soundly based on the concepts of statistical thermodynamics and the quasi-lattice model. The model has been verified for the systems electrolyte—water [25] and electrolyte—dimethyl sulfoxide [27] ( $\text{LiNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ) over the mole fraction range  $x_2 = 0.05$ — $0.30$ .

A further step in this field has been made by *Abraham* [28], who expressed the dependence of the excess molar volume on the activity of the solvent, i.e. on a quantity more readily accessible experimentally than is  $\Delta H_{tr}$ , which also reflects deviations from ideal behaviour.

$$V_m^E = x_1(1 - a_1) (Ax_1 + V_1^\infty - V_1^0) \quad (15)$$

where  $A$  is an empirical constant. A good fit of this equation to experimental data has been found for aqueous solutions of  $(\text{Ag}, \text{Tl})\text{NO}_3$ ,  $(\text{Cd}, \text{Ag}, \text{Tl})\text{NO}_3$ , and  $(\text{Li}, \text{K})\text{NO}_3$  over a range of water mole fractions from 0.10 to 0.55.

*Horsák* [29] has taken up the concept of the apparent molar volume of solvent and derived an equation for the molar volume of solution as a function of composition on the basis of the quasi-lattice model of solutions by assuming that water is distributed between the cationic and anionic sublattices in the ratio of the stoichiometric coefficients of electrolyte  $M_pX_q$ , i.e.  $p:q$ . Considering the probability of finding a solvent molecule in the immediate neighbourhood of an ion, he derived, for  $p = q = 1$ , the relation

$$V_m = x_2 V_2^0 + (1 - x_2) [V_1^\infty + ax_2/(1 + x_2)] \quad (16)$$

where the parameter  $a$  accounts for the change in solvent volume in the neighbourhood of an ion. Equation (16) describes adequately the behaviour of aqueous solutions of alkali metal chlorides and nitrates over the mole fraction range  $x_2 = 0$ — $0.4$ . This approach has been used as a mathematical expedient in correlating a large set of data by the use of a minimum number of parameters; however, it cannot be used in considerations of ion sizes and interactions in solutions, because the separation of the molar volume of electrolyte into ionic contributions is made on the basis of a nonthermodynamic assumption, as was the case with the apparent molar volumes of electrolytes in infinitely dilute solutions.

Mention should also be made of a study by *Claes and Gilbert* [30]. These workers assume that at a low content of solvent in solution there are only ion—solvent interactions as a result of which the volume of the solvent molecules is

changed to an extent characteristic of each electrolyte. This apparent molar volume of solvent is taken to be constant up to the point when the solvent content has reached a composition where solvent—solvent interactions start to become significant. In the range of validity of this approximation, the molar volume of solution can be expressed in the form

$$V_m = x_2 V_2^0 + x_1 V_1^0 \quad (17)$$

This equation has been confirmed by data for the systems  $\text{NH}_4\text{NO}_3 + \text{NH}_4\text{Cl} + \text{LiNO}_3 + \text{H}_2\text{O}$ ,  $\text{LiNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$ , and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O}$ . The last mentioned system has been treated by using an alternative approach in which a molten salt hydrate is considered as a chemical individuum and the water contained in it is not reckoned with in expressing the concentration of water in the system. This is not fully justified; for instance, the fact that some electrolytes form several crystalline hydrates or solvates alone suggests that the volumetric properties of solvent molecules in solutions involving such hydrates or solvates are not unequivocally defined. Yet, there are a number of studies based on this approach. By the molar volume of pure component in the sense of eqn (3) we understand in this case the molar volume of the molten hydrate or solvate. In calculating the volumetric properties, some authors [4, 13, 31] replace the molar volume by the equivalent volume. This approach relies on a study of the volumetric properties of anhydrous molten nitrates [32] which shows that the major contribution to the volume of molten alkali and alkali earth nitrates is the volume of the nitrate anion, while the small cations just fill the interstitial holes left in the anionic sublattice. The equivalent volume of a hydrate is calculated as the quotient of the molar volume of the hydrate and the oxidation number of the cation, and the volume of this "equivalent" is treated as the basic unit in studying the volumetric properties. However, this approach does not appear to be justified. For molten salt hydrates, it assumes the preferential formation of hydrated cations of a size greater than that of the nitrate anion, so that the contributions of the two ions to the total volume would be opposite to those in molten salts. Studies in this area check whether the additivity rule is obeyed, *i.e.* whether the behaviour of a ternary system treated as a pseudobinary one is described by eqn (2).

Experimental studies on a number of mixtures of two hydrates have established that the molar volume can be calculated on the basis of eqn (3) with the hydrates considered as components 1 and 2. Additivity of the molar volumes is considered as proof that the cations do not "compete" for water molecules and also that the hydrates involved do exist as structural units of the solutions. It must be realized that additive behaviour does not rule out a competition for water molecules provided that the volume of water molecules in the coordination sphere is the same for both ions. The additive behaviour has been found for the systems

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [30],  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  [33],  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  [31],  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  [31],  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  [34]. Deviations from additivity have been observed for the systems  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [35],  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [36], and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [4]. For the systems  $\text{ZnCl}_2 \cdot n\text{H}_2\text{O} + \text{LiCl} \cdot n\text{H}_2\text{O}$  ( $n=4-6$ ), *Easteal et al.* [37] ascribed the observed deviations from additivity to complex formation.

In testing the validity of eqn (3) for mixtures of hydrates and anhydrous electrolytes, a linear dependence of the molar volume on the concentration of anhydrous salt is taken as proof that the added electrolyte exerts no influence on the water molecules. Since the molar volumes of molten anhydrous salts at the temperature of measurement are unknown and in addition, molar volumes are usually measurable only for  $x_2 < 0.2$ , these studies are inconclusive. Examples of such systems are  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{TINO}_3$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{TINO}_3$  [38], and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$  [39].

Recent studies on the system  $\text{Zn}(\text{NO}_3)_2 + \text{dimethyl sulfoxide (DMSO)}$  have revealed an unusual composition dependence of the molar volume of solutions with a well-pronounced minimum at a mole fraction  $x_2 = 0.2$  [40]. A similar dependence has been observed for the systems  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ , and  $\text{Mg}(\text{NO}_3)_2 + \text{DMSO}$  [41]. In contrast with this, aqueous solutions of zinc nitrate show no irregularities in the composition dependence of the molar volume [14].

Studies on molar volumes have so far been concerned largely with expressing the composition dependence of the molar volume, the parameters in the equations used being correlated, at best, with some thermodynamic quantities. Only few authors, e.g. [42], so far have inquired into structural aspects that could be inferred from the volume changes measured as a function of composition or temperature. These questions might be elucidated in connection with other physical properties of electrolyte solutions, such as the molar refractivity or the relative permittivity, which give measures of the polarizability or the molar polarization of molecules, respectively, and are related directly to the molar volume. Considerable progress in the interpretation of the volumetric properties of highly concentrated solutions could be made by using evidence from spectroscopic studies (Raman, X-ray) which, unfortunately, are still very scanty.

### Symbols

$c$	molar concentration, amount of component 2 in 1000 cm <sup>3</sup> of solution	mol dm <sup>-3</sup>
$m$	molality, amount of component 2 per 1000 g of component 1 in solution	mol kg <sup>-1</sup>
$M_i$	molar mass of component $i$	g mol <sup>-1</sup>
$n_i$	amount of component $i$	mol

$t$	temperature	$^{\circ}\text{C}$
$V$	volume	$\text{cm}^3$
$V_i$	apparent molar volume of component $i$ ( $V_2 \equiv \Phi_V$ )	$\text{cm}^3 \text{mol}^{-1}$
$\bar{V}_i$	partial molar volume of component $i$	$\text{cm}^3 \text{mol}^{-1}$
$V_i^{\circ}$	molar volume of pure component $i$ in the liquid state	$\text{cm}^3 \text{mol}^{-1}$
$V_i^{\infty}$	partial molar volume of component $i$ at infinite dilution ( $x_i \rightarrow 0$ )	$\text{cm}^3 \text{mol}^{-1}$
$V_m$	molar volume of solution, <i>i.e.</i> volume of solution containing 1 mole of components	$\text{cm}^3 \text{mol}^{-1}$
$V_m^E$	excess molar volume	$\text{cm}^3 \text{mol}^{-1}$
$x_i$	mole fraction of component $i$ in solution	
$\rho$	density	$\text{g cm}^{-3}$
$\Phi_V$	apparent molar volume of electrolyte (component 2)	$\text{cm}^3 \text{mol}^{-1}$
$\Phi_V^{\infty}$	apparent molar volume of electrolyte at infinite dilution ( $x_2 \rightarrow 0$ )	$\text{cm}^3 \text{mol}^{-1}$

### Subscripts

- 1 solvent
- 2 electrolyte

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